C10G-E038

SHIMADZU
Excellence in Science

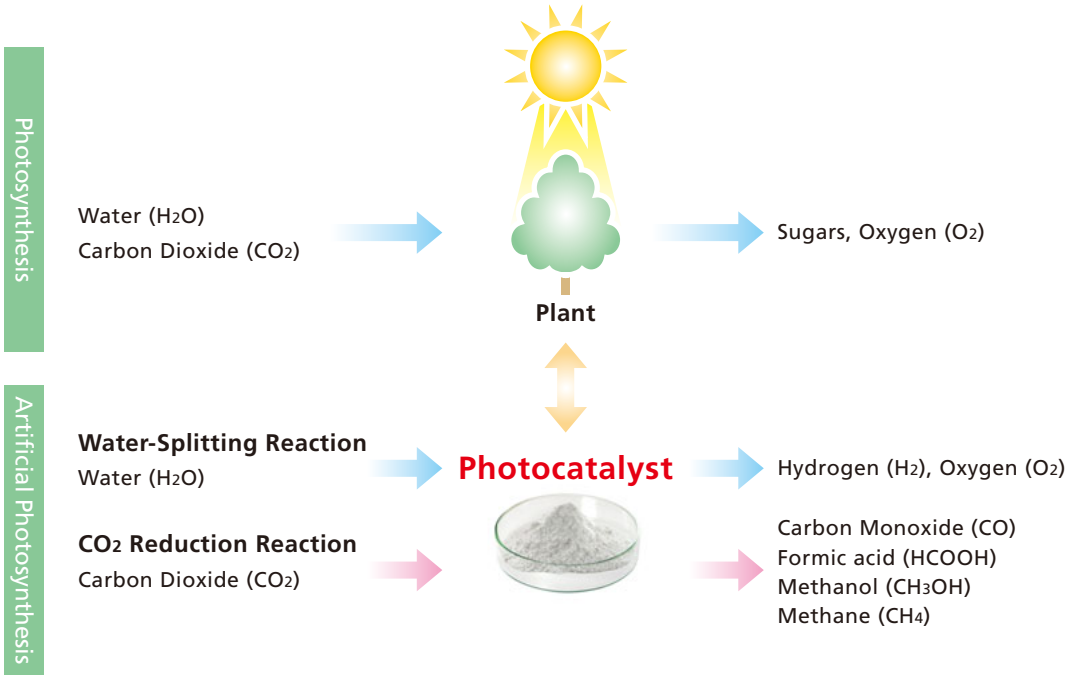
Analytical and Testing Instruments for Artificial Photosynthesis

Index

What is Artificial Photosynthesis?

Artificial photosynthesis is technology that uses a photocatalyst and sunlight to perform photosynthesis artificially. It allows converting light energy into useful compounds for use as a next-generation renewable energy source.

More specifically, it uses a water-splitting reaction to generate hydrogen (H_2) and oxygen (O_2) from water or uses a reduction reaction to generate organic compounds such as carbon monoxide (CO), formic acid (HCOOH), methanol (CH_3OH), and methane (CH_4) from carbon dioxide (CO_2). Artificial photosynthesis is a clean environmentally friendly technology that generates energy from ingredients such as water and carbon dioxide.



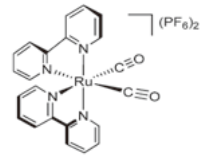
Artificial Photosynthesis Research

Semiconductor Catalyst Systems (Heterogeneous Systems)

These systems use oxides or nitrides of titanium (Ti), tantalum (Ta) or other metals as photocatalysts. Because they do not dissolve uniformly in solution, they are referred to as heterogeneous catalysts. There is a wide variety of types with different reactivity. In an effort to develop a photocatalyst with higher reaction efficiency, a variety of structures have been studied.

Supermolecular Systems (Homogenous Systems)

These systems use metal complexes or supermolecular metal complexes of ruthenium (Ru), rhenium (Re) or other metals as photocatalysts. Because they dissolve uniformly in solution, they are referred to as homogeneous catalysts.



Example of Homogeneous Photocatalyst

Hybrid Systems (Hybrid of Semiconductor and Supermolecular Metal Complex Systems)

Hybrid systems improve reaction efficiency by using a combination of semiconductor materials and (supermolecular) metal complexes.

Biological Systems

Biological systems use the photosynthesis reaction of bacteria, algae, or other organisms.

Analysis of CO Generated from CO_2 Reduction Reactions (GC)

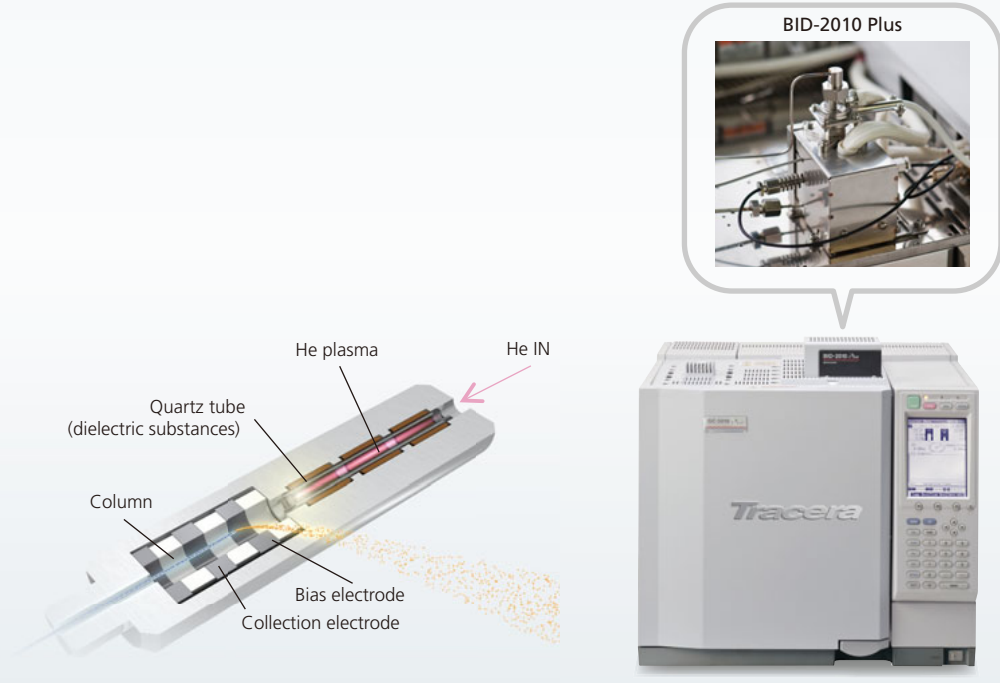
The photochemical CO_2 reduction reaction using a photocatalyst generates CO as a reaction product. The catalyst performance can be evaluated by determining the quantity of CO generated during a given unit period.
This measurement is normally performed using GC. In the following example, a Tracera (GC-BID) system is used to measure the CO in reaction products.

Analytical Conditions

Gas chromatograph	: Tracera (GC-2010 Plus A + BID-2010 Plus)
Column	: Micropacked ST (2 m × 1 mm I.D.)
Column temp.	: 35 °C (2.5 min) – 20 °C/min – 180 °C (0.5 min), total 10.25 min
Carrier gas control	: Pressure
Pressure program	: 250 kPa (2.5 min) – 15 kPa/min – 360 kPa (0.42 min) (He)
Injection mode	: Split (1:10)
Injection port temp.	: 150 °C
Detector temp.	: 280 °C
Plasma gas flowrate	: 70 mL/min
Injection volume	: 50 µL

Tracera High Sensitivity Gas Chromatograph System

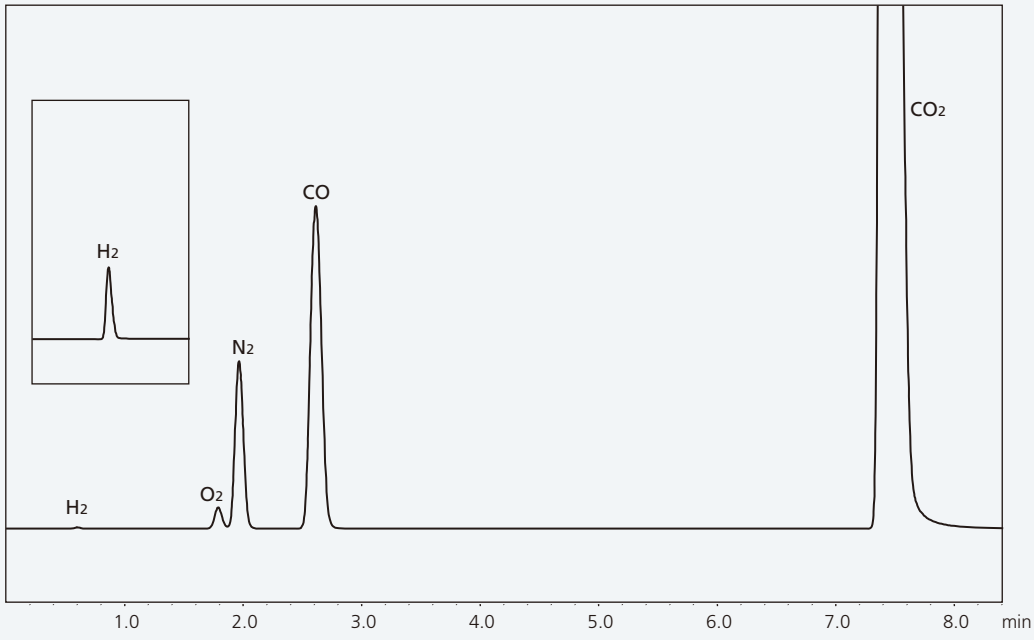
The barrier discharge ionization detector (BID) generates a He (helium) plasma by applying a high voltage to a quartz glass tube. Then the light energy from the He plasma ionizes the compounds eluted from the column and the ions are collected using a collection electrode and output as peaks. Due to the extremely high 17.7 eV light energy of the helium, the BID is able to detect with high sensitivity a variety of compounds other than neon (Ne), which has a higher ionization energy than helium, and helium, which is a plasma gas, making it a truly next-generation general-purpose plasma detector.



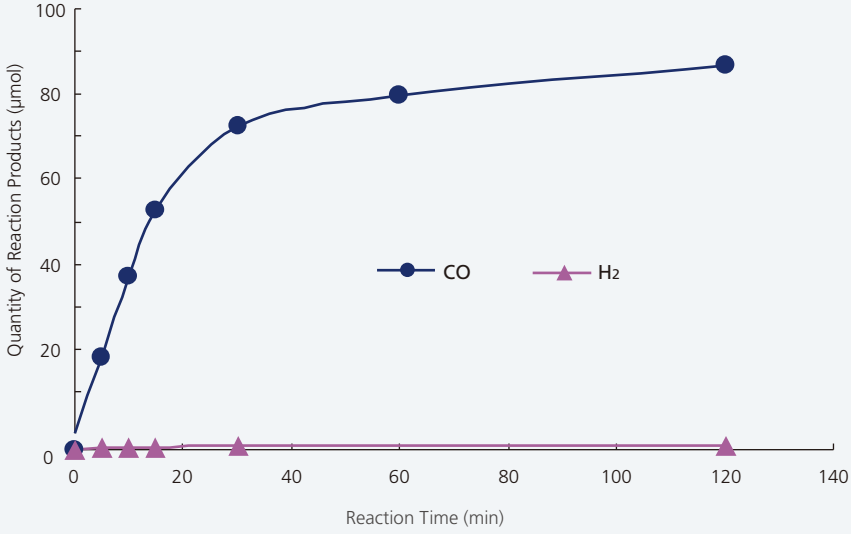
Tracera (GC-BID)

Analytical Data

CO and also H_2, O_2, and N_2 were all measured simultaneously with high sensitivity.
The BID allows measuring all sorts of components, except for helium and neon to obtain a wide variety of information with a single measurement.



Chromatogram of Components in Gas Phase of Photochemical CO_2 Reduction Reaction



Quantity of CO and H_2 Generated Versus Reaction Time

Source: Associate Professor Hitoshi Ishida and Assistant Professor Yusuke Kuramochi, School of Science, Kitasato University, Japan Science and Technology Agency (JST), PRESTO

Analysis of Formic Acid Generated from CO_2 Reduction Reactions (GC)

The photochemical CO_2 reduction reaction using a photocatalyst generates formic acid as a reaction product.
Normally instruments such as liquid chromatographs, ion chromatographs, or capillary electrophoresis systems are used to analyze formic acid. However, analyzing the formic acid dissolved in organic solvents requires diluting the solution by at least a factor of ten, with water or mobile phase, which makes it difficult to analyze low concentrations in some cases.
However, gas chromatography (GC) allows measuring organic solvents directly without dilution. Furthermore, using a BID detector, which is capable of detecting formic acid with high sensitivity, allows analyzing concentrations down to ppm levels.
This example describes using a GC-BID system to analyze formic acid in organic solvent.

Analytical Conditions

Gas chromatograph	: Tracera (GC-2010 Plus A + BID-2010 Plus)
Column	: RESTEK Rtx-WAX (60 m × 0.53 mmI.D., df = 1.0 µm)
Column temp.	: 80 °C – 5 °C/min – 130 °C – 15 °C/min – 230 °C (3 min)
Carrier gas	: He at 50 cm/sec (constant linear velocity)
Injection mode	: Split (1:2)
Injection port temp.	: 240 °C
Detector temp.	: 240 °C
Plasma gas flowrate	: 50 mL/min
Injection volume	: 1 µL

Sample Pretreatment Using Cation-Exchange Cartridge

If samples (or reaction solutions) contain salts or other contaminants, they must be removed by pretreatment. In this case, a cation-exchange cartridge was used to pretreat an actual sample with 0.1 M dissolved NEt_4BF_4.

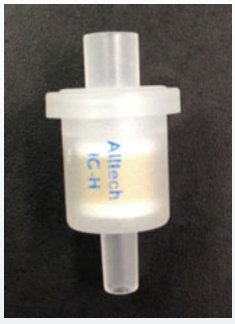
Cartridge conditioning — 5 mL DMA at 2 mL/min or less

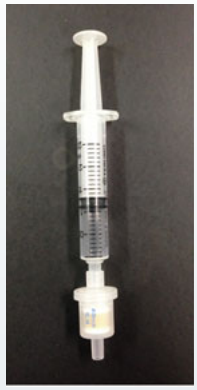
↓

Inject sample — 3 mL (dispose of 2 mL and recover 1 mL) at maximum 1 mL/min

↓

GC analysis

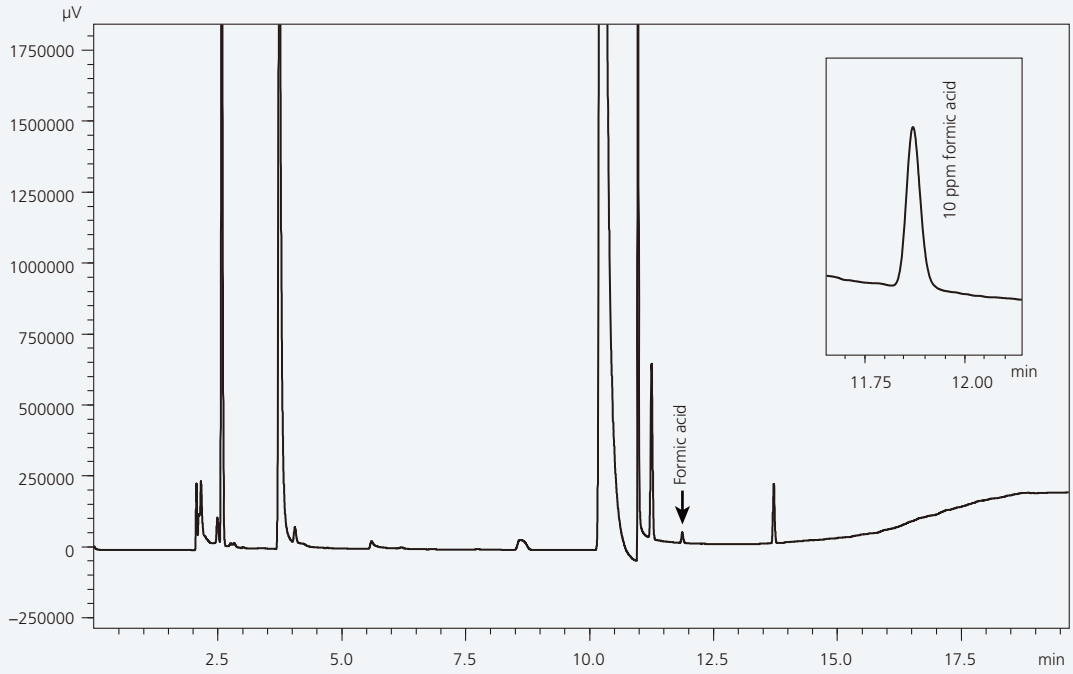




Alltech Maxi-Clean 0.5 mL IC-H
50 pk P/N: 30264
Strong cation exchange
Retention volume 1.9 meq/mL, which allows processing about 9 mL, given a sample containing 0.1 M of a monovalent salt

Analytical Data

10 ppm of formic acid in the actual sample was detectable with high sensitivity.



Chromatogram After Pretreating Actual Sample (DMA solvent and 0.1 M NEt_4BF_4)

Sample source: Professor Osamu Ishitani, Graduate School of Science and Engineering, Tokyo Institute of Technology

When conducting GC measurement of formic acid at low concentrations, care must be taken to prevent adsorption to the various component surfaces. To prevent adsorption at the injection port and column, phosphoric acid treatment of the glass insert and column is conducted. Detailed information can be found in Shimadzu Application News G279.

Also, if samples (or reaction solutions) contain salts or other contaminants, they must be removed by pretreatment prior to GC measurement. Because it is considered that the adsorption of formic acid in the GC injection unit is due to accumulation of salts which coexists with the sample in the injection unit. Detailed information can be found in Shimadzu Application News G280.

Confirmation of Reaction Mechanism Using $^{13}CO_2$ (GC-MS)

The photochemical CO_2 reduction reaction using a photocatalyst generates CO as a reaction product.
It is necessary to confirm whether the resulting CO was generated from the CO_2 reduction reaction, as predicted, or entered the reaction system or was generated from another source.
The occurrence of an expected reaction can be confirmed by causing a reduction reaction using $^{13}CO_2$ labeled with ^{13}C and measuring the resulting ^{13}CO with a GC-MS system.
This example describes ^{13}CO measurements using a GC-MS system.

Analytical Conditions

GC-MS	: GCMS-QP2010 Ultra
Column	: RT®-Msieve 5A (30 m L, 0.32 mm I.D., df = 30 µm, RESTEK P/N 19722) + Rtx®-1 (5 m × 0.25 mmI.D., df = 0.5 µm, particle trap)
[GC]	
Injection unit temp.	: 200°C
Column oven temp.	: 35 °C (2 min) → (10 °C /min) → 150 °C (5 min)
Injection mode	: Split (50:1)
Control mode	: Pressure (100 kPa)
Carrier gas	: Helium
Injection volume	: 100 µL (injected using a gas-tight syringe)
[MS]	
Interface temp.	: 200°C
Ion source temp.	: 200°C
Measurement mode	: Scan
Measurement range	: *m/z* 10 to 100
Event time	: 0.3 sec
Ionization method	: EI
Ionization voltage	: 70 eV
Emission current	: 150 µA

GCMS-QP2010 Ultra Gas Chromatograph Mass Spectrometer

GCMS-QP2010 Ultra model features a newly designed electronic control platform that achieves the fastest scan speeds in their class.
Furthermore, improved functionality allows shorter analytical cycle times and faster GC maintenance, increasing analytical productivity in the laboratory.
In addition, an ECO mode reduces the power and carrier gas consumption when in standby mode, lowering operating costs and the environmental impact.

Analytical Data

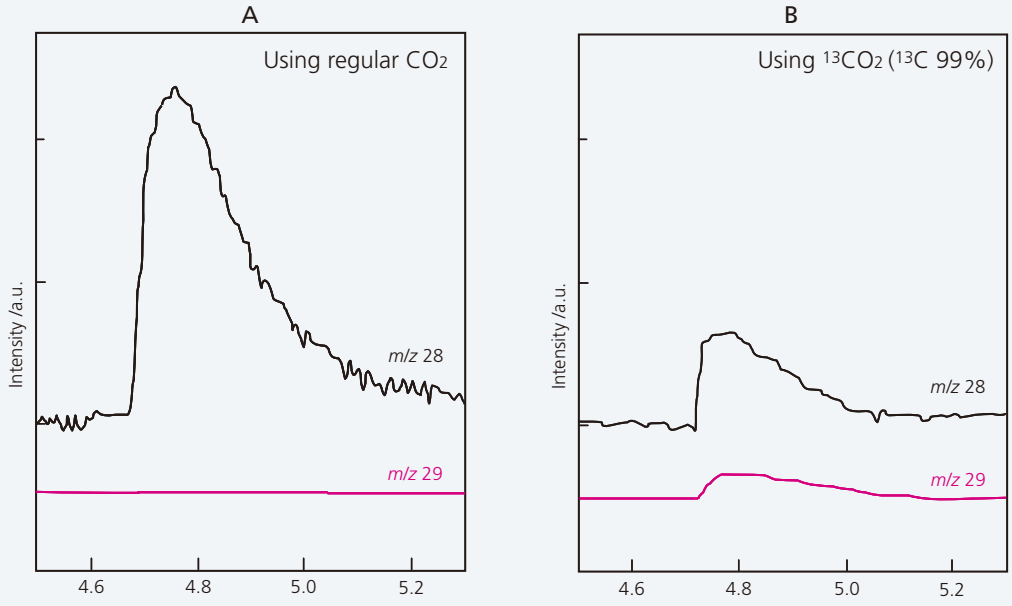


Fig. 1 Extracted Ion Chromatogram from Measuring Photocatalyst Reaction Products in Gas Phase Sample
(A) Experiment using regular CO_2 (B) Experiment using $^{13}CO_2$

A is an extracted ion chromatogram of CO obtained with an experimental system using unlabeled CO_2 (methanol solvent), whereas B was obtained using $^{13}CO_2$ (methanol solvent). B shows a peak at *m/z* 29 (^{13}CO), but it also shows a peak at *m/z* 28 (CO). Therefore, it indicates that the CO generated from CO_2 in this reaction is only a portion of the total CO.

Source: Professor Osamu Ishitani, Graduate School of Science and Engineering, Tokyo Institute of Technology

Sekizawa, K; Maeda, K; Domen, K; Koike, K; Ishitani, O. *J. Am. Chem. Soc.,* 2013, *135,* 4596.
Artificial Z-Scheme Constructed with a Supramolecular Metal Complex and Semiconductor for the Photocatalytic Reduction of CO_2

Simultaneous Analysis of Formic Acid and Formaldehyde (HPLC)

Some reaction systems using photocatalysts simultaneously produce both formic acid and formaldehyde in the reaction solution. This example describes using a Shimadzu organic acid analysis system to analyze formic acid and other organic acids based on the pH buffering method and simultaneously analyze formaldehyde using a differential refractive index detector.

Analytical Conditions

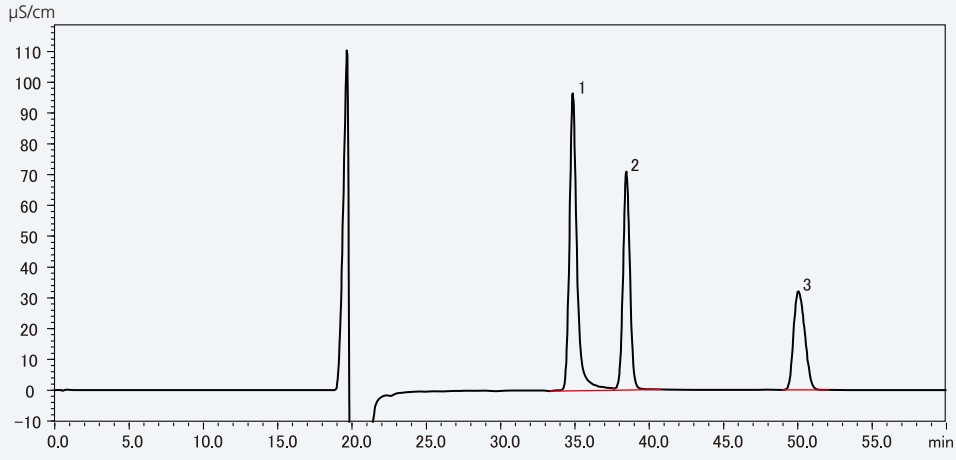
Column	: YMC Hydrosphere C18 (150 mmL. × 4.6 mmI.D.)
	Shim-pack SCR-102H (300 mmL. × 8.0 mmI.D.) × 2
Mobile phase	: 5 mmol/L Perchloric Acid
Flowrate	: 0.6 mL/min
Column temp.	: 40°C
Reaction reagent	: 5 mmol/L Perchloric Acid
	20 mmol/L Bis-Tris
	0.1 mmol/L EDTA-4H
Flowrate	: 0.6 mL/min
Reaction temp.	: 40°C
Detectors	: Electrical conductivity and reflective index
Injection volume	: 100 µL

Nexera X2 Ultra High Performance Liquid Chromatograph

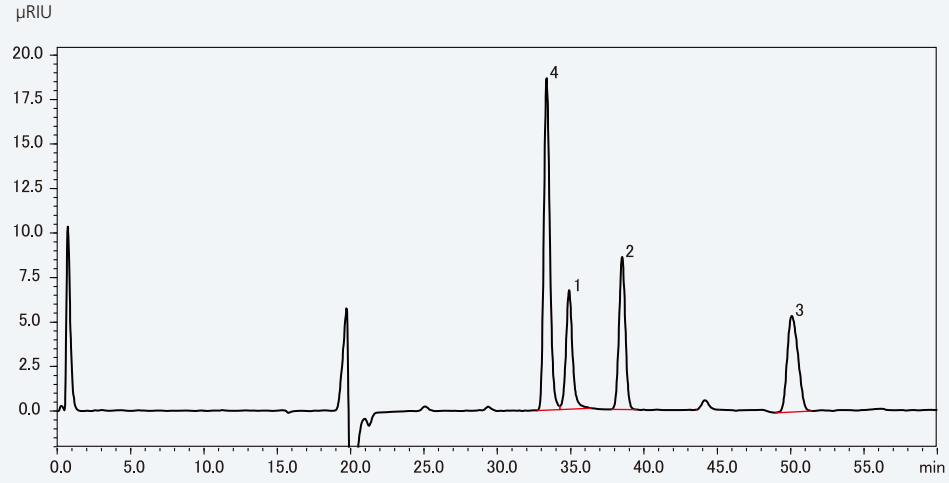
Maximizing the Potential of UHPLC/HPLC Analysis

The Nexera X2 is a UHPLC system that is even more advanced than the Nexera. The flexible system design achieves a true fusion between UHPLC and HPLC, which means the Nexera X2 can be used for a much broader range of applications.
The Nexera X2 is a completely new UHPLC system that offers the highest levels of speed, sensitivity, separation, stability, and reliability.

Analytical Data



Analysis of Organic Acids Using an Electrical Conductivity Detector



Peaks:
1. Formic Acid
2. Acetic Acid
3. Propionic Acid
4. Formaldehyde

Analysis of Formaldehyde and Organic Acids Using a Differential Refractive Index Detector

Shimadzu's organic acid analysis system is often used to analyze organic acids based on the pH buffering method, which offers superior separation and selectivity. However, the Shim-pack SCR-102H ion-exclusion column used with that system results in overlapping between formic acid and formaldehyde peaks. Therefore, a reversed-phase YMC Hydrosphere C18 column was added to improve separation.

In addition, because formaldehyde cannot be detected with an electrical conductivity detector, a differential refractive index detector was also connected in series.

The figures show an example from analyzing a standard sample containing a few hundred ppm of each component. Note that differential refractive index detectors are inferior to other detectors both in terms of sensitivity and selectivity.

Analysis of Hydrogen Peroxide (HPLC)

In some cases hydrogen peroxide is produced in reaction systems using photocatalysts.
To analyze hydrogen peroxide in reaction solutions with high sensitivity, it is useful to use an HPLC system equipped with an electrochemical detector (ECD).
In this example, hydrogen peroxide is detected with high sensitivity in water.

Analytical Conditions

Mobile phase	: 50 mmol/L sodium sulfate + 100 µmol/L aqueous EDTA 2Na solution
Column	: Inertsil CX (250 mmL. × 4.6 mmI.D., 5 µm)
Flowrate	: 0.8 mL/min
Injection volume	: 10 µL
Column temp.	: 40°C
Detector	: Eicom-ECD + 500 mV vs. Ag/AgCl 1.0 sec time constant, 25 °C
Standard sample	: Hydrogen peroxide (30 % aqueous hydrogen peroxide), Wako Pure Chemical Industries super special grade
Concentration of standard samples for calibration curve	: 0.001, 0.004, 0.04, 0.4, 4 mg/L (prepared with mobile phase)

HPLC Equipped With Electrochemical Detector (ECD)

Nexera X2

Eicom Brand

ECD-700S / ATC-700

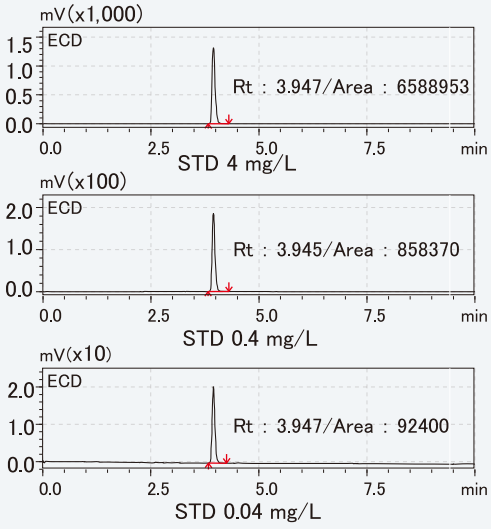
Electrochemical detectors use a redox reaction. Due to high selectivity, it is able to detect target components with high sensitivity even in samples with large numbers of contaminants.

* ECD-700S/ATC-700 may not be sold in your country. Please contact us to check the availability in your country.

Materials provided by:
EiCOM

Analytical Data

Chromatograms

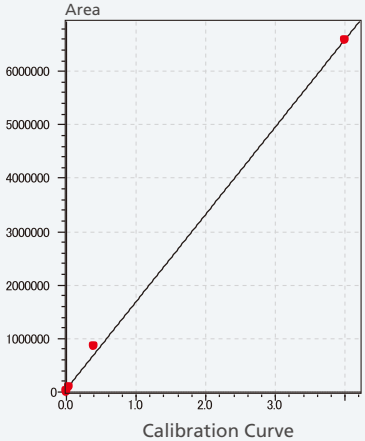


Chromatograms for Different Concentrations

Summary of Results

Level	Conc.	Avg. Area	Area %RSD	Area 1	Area 2	Area 3
1	4	6584697	0.076	6579170	6585967	6588953
2	0.4	856046	0.399	852120	857648	858370
3	0.04	92544	0.177	92722	92509	92400
4	0.004	13715	0.265	13713	13752	13679
5	0.001	7873	0.324	7858	7902	7859

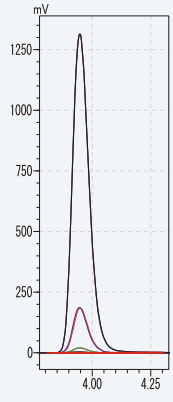
Calibration Curve



Calibration Curve

Calibration Curve Information
Y = aX + b
a = 2.18074e+006
b = 52520.7
R^2 = 0.9991648
R = 0.9995823

External standard method
Calibration curve: Straight line
Intercept at origin: No
Weighted: No



Chromatograms for Different Concentrations (Overlaid)

Hydrogen peroxide was measured with high sensitivity in water at µg/L level concentrations. The results showed good linearity and reproducibility.

Light Irradiation In-Situ Measurement of Semiconductor Photocatalyst (SPM)

In addition to observing the shape of micro areas of a sample surface, scanning probe microscopes (SPM) can also be used to acquire various information about the properties of the surface, such as phase, magnetic force, and viscoelasticity.
In this example, the electrical potential on a surface irradiated with light was measured to determine the excitation level of a photocatalyst.

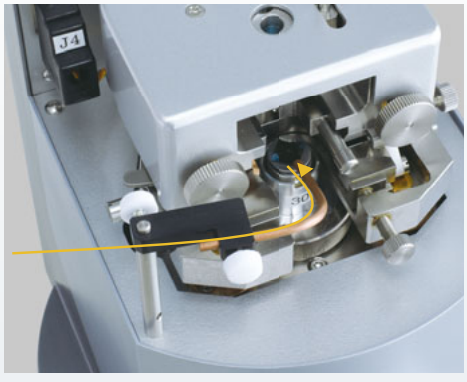
Measurement Conditions

Instruments : SPM-9700 and light irradiation unit (top surface irradiation)
Atmosphere : Atmospheric air
Scan speed : 0.3 Hz
Pixels : 256 × 256
Mode : KFM
UV exposure : Ozone-free mercury-xenon lamp, 300 to 450 nm

SPM-9700 Light Irradiation-Scanning Probe Microscope System

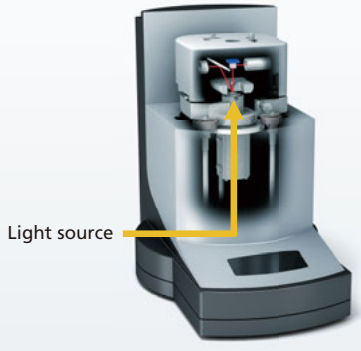
SPM-9700

Light Irradiation-Scanning Probe Microscope System allow observing the shape of surfaces and measuring surface properties with the surface illuminated with light. Because it allows performing in situ measurements while illuminated, it can be used to analyze the sample that is absorbing light, such as to measure the photocatalyst excitation status or electrical generation status of solar cells. Therefore, it is ideal for monitoring and evaluating changes in sample status in response to photoirradiation.



Light Irradiation Unit
(Top Surface)

Optical fiber is routed to the sample surface to illuminate it with light from above.

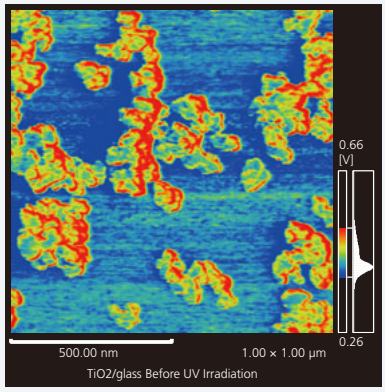


Sample Bottom Surface Laser Illumination Kit
(Bottom Surface)

Irradiated light is introduced via various external sources, such as laser, high-pressure mercury lamp, or LED.

Measurement Data

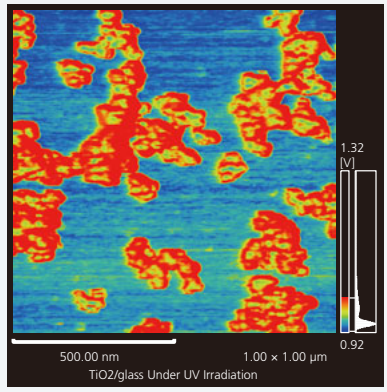
Surface Potential Image



Surface Potential Image Before UV Irradiation
200 mV Average Difference in Potential Between
Glass Substrate and Catalyst Particles

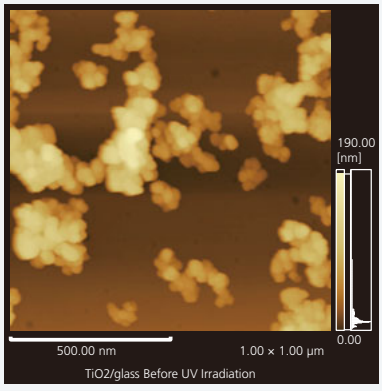
UV irradiation

Surface potential changed significantly by UV irradiation.



Surface Potential Image Under UV Irradiation
330 mV Average Difference in Potential Between
Glass Substrate and Catalyst Particles

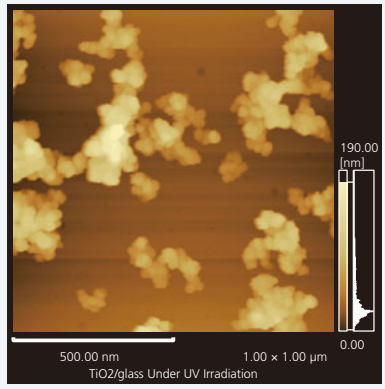
AFM Profile Image



AFM Profile Image Before UV Irradiation

UV irradiation

The profile did not change by UV irradiation.



AFM Profile Image Under UV Irradiation

Platinum supported titanium (TiO_2) microparticles used as semiconductor catalysts were secured to a glass substrate and then the surface potential and shape were observed using a scanning probe microscope (SPM).
The left image was obtained in atmospheric air, whereas the right image was obtained from the identical location illuminated with UV light from above.
In the atomic force microscope (AFM) 3D contour images (lower left and right), the shape of the catalyst particles does not change by UV irradiation.
However, the surface potential images (upper left and right) indicate that the surface potential of the catalyst particles increases by an average 130 mV after exposure to UV light, which was a reversible change. This indicates that charge separation occurs at the catalyst surface by photoirradiation.

Sample source: Associate Professor Kazuhiko Maeda, Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology

Band Gap Measurement of Titanium Oxide (UV)

Photocatalysts provide catalytic effects when they absorb light and become excited. Because each photocatalyst has a characteristic band gap, they are excited in different wavelength regions.
Since UV-visible absorption spectra are used to confirm the excitation wavelengths, they serve as the most fundamental of tools for evaluating photocatalysts.
In this example, the band gap of titanium oxide was measured using a UV spectrophotometer.

Measurement Conditions

Instruments used	: UV-2600 UV-VIS Spectrophotometer ISR-2600 Plus Integrating Sphere Attachment
Measurement wavelength range	: 200 to 1400 nm
Scan speed	: Medium
Sampling pitch	: 1.0 nm
Photometric value	: Reflectance
Slit width	: 5 nm
Detector switchover wavelength	: 830 nm

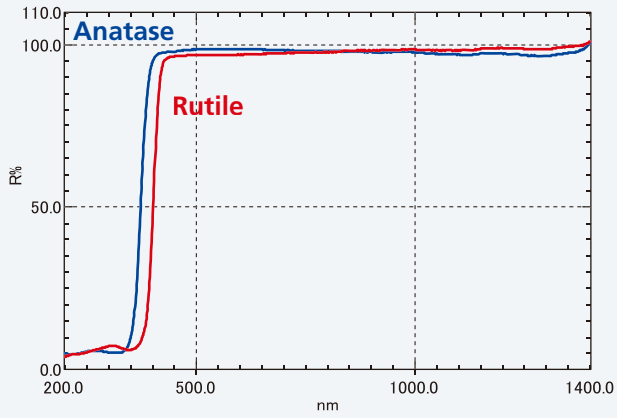
Titanium oxide, which is a material typically used in photocatalysts, has three types of crystal structures— anatase, rutile, and brookite forms. Each type has different density, refractive index, and other properties.
The band gap was determined for anatase and rutile type titanium oxide powders, the types mostly commonly used for industrial applications, by measuring the diffuse reflectance.

UV-2600 UV-VIS Spectrophotometer

- Featuring a compact size and a proprietary Lo-Ray-Ligh grade diffraction grating, the UV-2600 achieves especially high efficiency and low stray light levels.
- The ISR-2600 Plus integrating sphere unit includes two detectors, a photomultiplier tube and InGaAs detector, for high sensitivity measurement capability over a wavelength range from 220 to 1400 nm.
- Combination of the UV-2600 and ISR-2600 Plus, which allows measuring wavelengths ranging from UV to near infrared, is ideal for evaluating the wavelengths absorbed by photocatalysts.

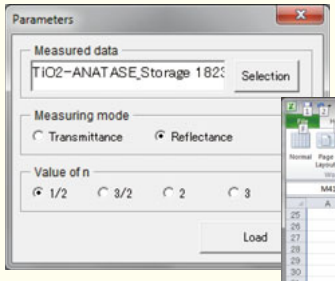
UV-2600 + ISR-2600Plus

Analytical Data

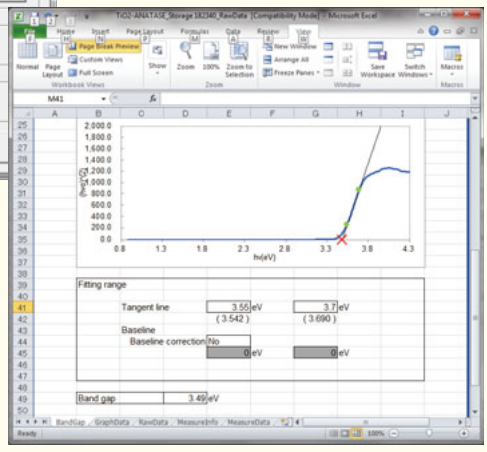


Diffuse Reflectance Spectra of Titanium Oxide

Excel Macro Program for Calculating Band Gap



Settings Window



Calculation Results Window

BandGap Calculation Results
Rutile: 3.20 eV
Anatase: 3.49 eV

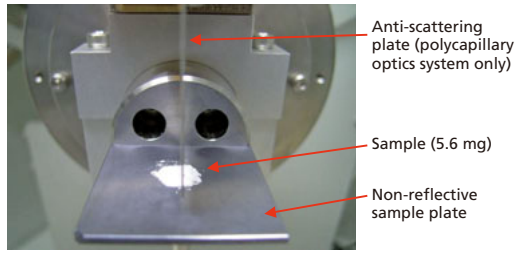
The band gap was determined from the diffuse reflectance spectra. The Excel band gap calculation macro is used by loading spectral data, selecting [Measuring mode (Transmittance/Reflectance)] and [Value of n] (type of transition process), and then specifying the range that can be approximated as a straight line near the inflection point as the tangent line. This makes it easy to determine the band gap value using a Tauc plot.

Measurement of Trace Semiconductor Photocatalyst Powder (XRD)

Semiconductor photocatalysts such as metal oxides and nitrides are identified, qualified, or their crystallinity evaluated using X-ray diffractometers (XRD).
XRD results show diffraction patterns that are plotted with diffraction angle on the horizontal axis and diffraction intensity on the vertical axis. Then these patterns are compared to the diffraction patterns for known substances for identification and qualification. However, because the sample surface shape can affect diffraction pattern results, sufficient sample quantity is generally required for powder samples, so that a flat surface can be formed for measurement.
However, polycapillary parallel beam optics system reduces such problems and enables high measurement sensitivity and precision even with small sample quantities.
In this example, multiple semiconductor photocatalysts were measured and compared.

Measurement Conditions

Item	Polycapillary Optical System	Focused Beam Optical System
Instruments	XRD-7000	XRD-7000
Goniometer Radius	200 mm	200 mm
X-Ray Source	LFF Cu tube + polycapillary	LFF Cu tube
Tube Voltage/Current	40 kV / 40 mA	40 kV / 40 mA
Anti-Scattering Plate Height	4 mm	None
Slit	None	DS 1 deg., SS 1 deg., RS 0.3 mm
Monochromator	Yes	Yes
Stage	Standard sample stand	Standard sample stand
Scan Range	5 to 35 deg	5 to 35 deg
Scan Step Size	0.02 deg	0.02 deg
Scan Speed	2 deg/min	2 deg/min
Integration Time	0.6 sec/step	0.6 sec/step

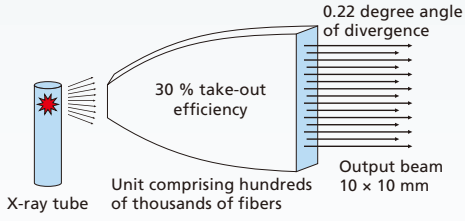


Powder Sample on
Non-Reflective Sample Plate

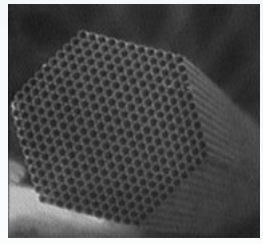
XRD was used to measure $KCa_2Nb_3O_{10}$, which is a layered ion-exchange material comprising calcium niobate perovskite layers and potassium ion layers, used as a semiconductor photocatalyst.
5.6 mg of the powder sample was placed on the non-reflective sample plate for measurement.

XRD Polycapillary Optics System

XRD-7000



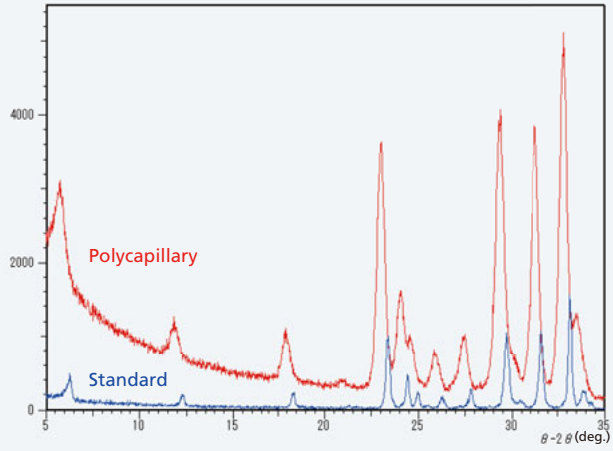
Polycapillary Parallel Beam Optics System



SEM Image

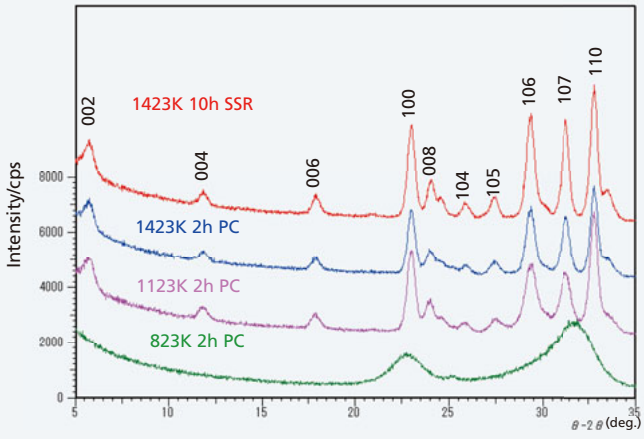
Polycapillaries are multiple narrow glass tubes used to guide X-rays. These capillary tubes guide the X-rays emitted from a point-source at a very high solid angle into parallel beams at the output port on the opposite end.
Compared to a standard optics system (Bragg–Brentano method), this system utilizes the X-rays emitted from the X-ray tube more efficiently, which allows achieving higher diffracted X-ray intensities. Furthermore, because the optical system uses parallel beams, the diffraction angle remains unchanged even if the sample measurement surface shift positions. Consequently, it resolves problems that standard optics systems can have with separation of diffracted rays or angle shifting and it allows measuring small quantities of powder samples without a flat surface or curved samples with high sensitivity and precision.

Analytical Data



Diffraction Pattern from Polycapillary and Focused Beam Optical Systems

The figure shows results from using polycapillary and standard optics systems to measure $KCa_2Nb_3O_{10}$ powder synthesized by baking at 1423 K for 10 hours using the SSR (solid state reaction) method.
The polycapillary optics system resulted in about three times higher intensity levels than the standard optics system, where the error in 2θ due to sample status (height) is assumed to be small.



Diffraction Patterns for $KCa_2Nb_3O_{10}$ Powder Samples Prepared Using Different Synthesis Parameters

The figure shows results from using the polycapillary optics system to measure $KCa_2Nb_3O_{10}$ powder samples prepared using four different synthesis conditions. At 823 K, the peaks are much broader than the other three samples, which indicates low crystallinity. Based on the measurement results for the samples synthesized using the PC (polymerized complex) method at 1123 K for 2 hours and at 1423 K for 2 hours, increasing the heating temperature resulted in a smaller FWHM value, which is presumably due to higher crystallinity. The results also showed a difference in FWHM between 1423 K 2-hour PC and 1423 K 10-hour SSR methods, which confirms that the differences in synthesis parameters affected crystallinity.

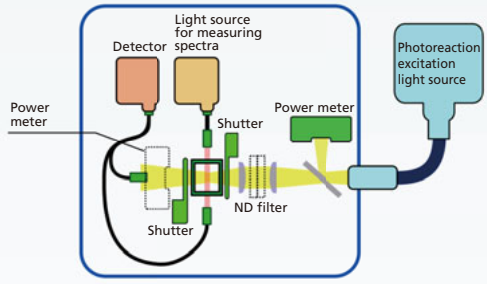
Sample source: Associate Professor Kazuhiko Maeda, Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology

Evaluation of Photoreaction Quantum Yield of Supermolecular Complex (QYM)

The photoreaction quantum yield is one performance indicator for photochemical reactions or photocatalysts. It is the ratio between the number of reaction product molecules from a photochemical reaction (or alternatively the reduction in number of molecules in the substrate) and the number of photons absorbed.
Conventionally, chemical actinometers based on substances with known quantum yield, such as iron oxalate, were used. However, this method requires performing experiments for long periods in a dark room by skilled personnel and also requires repeating the experiments if irradiation parameters are changed. It also has other problems, such as not being able to compensate for changes in light absorption by samples due to reactions.
Therefore, we developed the QYM-01 photoreaction quantum yield evaluation system which permits accurate and easy quantitation measurements of absorbed photons in conjunction with Professor Osamu Ishitani, Graduate School of Science and Engineering, Tokyo Institute of Technology.
In this example, we confirmed how results from the new system correlate with the conventional method.

QYM-01 Photoreaction Quantum Yield Evaluation System

QYM-01



QYM-01 Overview

Allows continuous measurement of UV-VIS absorption spectra during photoreactions
Capable of sample cell temperature control, sample solution stirring,
and automatic excitation light shuttering

Accurately and Easily measurement of the number of photons absorbed by Sample Solutions Allows simultaneously measuring changes in UV-VIS absorption spectra in photoreaction solutions

Features

Accommodates a wide range of photoreaction excitation light conditions (wavelength and light level).

- Allows changing the excitation wavelength and measuring the number of absorbed photons anywhere between 250 nm to 800 nm.
- The excitation light level can be adjusted and set by adjusting the number of photons irradiated.

Easy Measurements

- Includes a built-in spectrometer which has been calibrated using a NIST (National Institute of Standards and Technology)-traceable actinometer of which absolute light quantity is managed.
- Eliminates the need for calibration using a chemical actinometer.
- The excitation light level and wavelength switching is controlled via computer software.
- Includes simple computer software. Measures the number of photons using optimal measurement parameters.

Supports accurate measurements.

- Simultaneous UV-VIS absorption spectra measurement capability, a correction function for changes in the light level of the excitation light source, and other features ensure the number of absorbed photons can be measured accurately.
- Displays the photo count in real time. Allows confirming the current measurement status.

The QYM-01 was developed jointly with Ishitani–Maeda Laboratory, Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology.

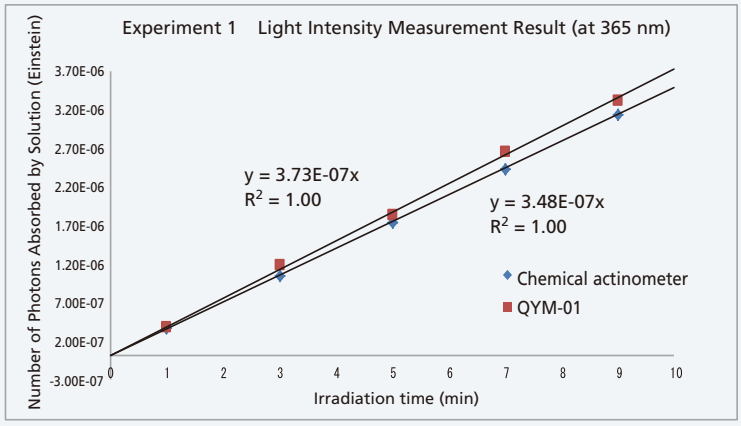
Analytical Data

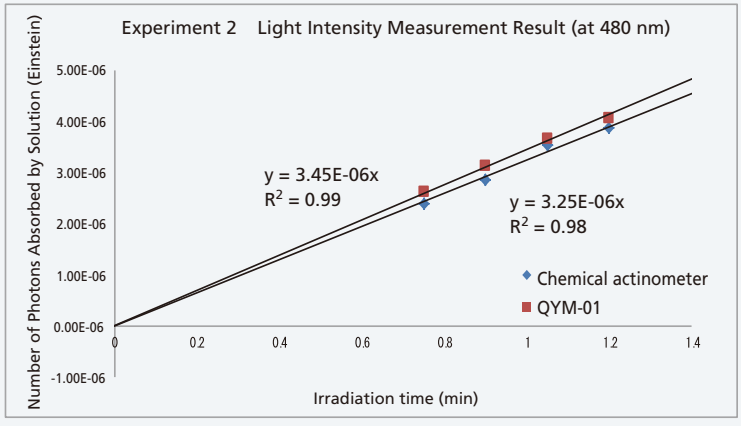
Comparison of QYM-01 and Chemical Actinometer (Iron Oxalate) by Measuring Light Intensities

The QYM-01 was verified by comparing measurements of the absorbed light intensity by the QYM-01 and a chemical actinometer. The QYM-01 was used to irradiate an aqueous potassium trioxalatoferrate (III) sample with photoreaction excitation light and measure the photons absorbed. Then the number of photons absorbed was determined from the amount of iron (II) produced in solutions with different irradiation periods in accordance to the relevant section in the fifth edition of "Jikken Kagaku Koza" (Series of Experimental Chemistry), published by the Chemical Society of Japan.

Experiment Conditions

	Experiment 1	Experiment 2
Excitation Light Wavelength	365 nm (Xenon lamp)	480 nm (Xenon lamp)
Sample Concentration	6 mM	150 mM
Photon Yield (value indicated in the fifth edition of "Jikken Kagaku Koza")	1.22	0.94





Number of Absorbed Photons

	Number of Absorbed Photons (Einstein/s)	
	Experiment 1	Experiment 2
Chemical Actinometer	5.84×10^{-9}	5.40×10^{-8}
QYM-01	6.19×10^{-9}	5.78×10^{-8}

Source: Ishitani–Maeda Laboratory, Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology.

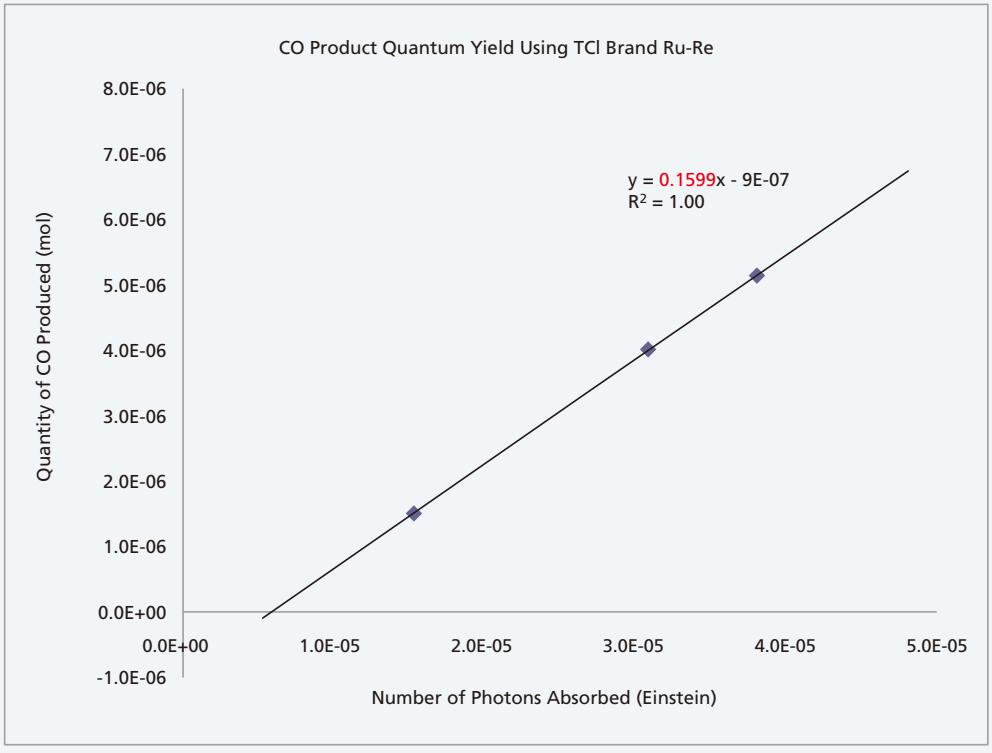
Analytical Data

Measurement of Quantum Yield of CO_2 Reduction Reaction by Ru-Re Supermolecular Complex Photocatalyst

We measured the quantum yield of a carbon dioxide reduction reaction by a Ru-Re supermolecular complex photocatalyst. Absorbed photons were measured using the QYM-01 and the amount of carbon monoxide generated from the reduction reaction was quantitated using a gas chromatograph. The quantum yield reported for carbon monoxide assuming the experimental conditions used was 0.15[1]. The experiment resulted in a quantum yield of 0.16.

Experiment Conditions

Photocatalyst	Ru-Re (FPh) (From Tokyo Chemical Industry, Product No. R0100, used without purification)	
Reaction Conditions	Photocatalyst	Ru-Re (FPh) (0.3 mM)
	Donor reducing agent	BNAH (0.1 M)
	Solvent	DMF-triethanolamine (5:1 v/v solvent mixture)
	Solution volume	4 mL
	Irradiation light	480 nm xenon lamp
	Reaction vessel	Quartz cell with branch (4 polished windows) (11 mL volume, 7 mL gas phase, 4 mL liquid phase)
Operating Procedure	Transfer the prepared solution to the 4-sided quartz cell with branch using a 4-mL transfer pipette. Bubble with CO_2 for 30 minutes and then seal the cell with a septum (prepare 3). Then after irradiating with light for 1, 2, or 2.5 hours, use a gas-tight syringe to acquire 100 µL of gas from the gas phase and quantitate the CO by GC.	



Quantum Yield Measurement Result	0.16
Reference Document	0.15

References 1) Y. Tamaki, K. Watanabe, K. Koike, H. Inoue, T. Morimoto, O. Ishitani, *Faraday Discuss.* 2012, 155, 115.

Source: Ishitani–Maeda Laboratory, Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology.

Particle Size Measurement of Titanium Oxide (Particle Size Analyzer)

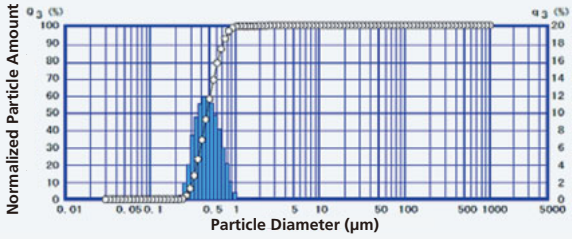
Reactions that generate hydrogen, formic acid, or other products, in artificial photosynthesis with photocatalysts occur at the surface of the photocatalyst. Therefore, an understanding of the particle size distribution is needed for evaluating reaction efficiency and other purposes.
In addition, semiconductor photocatalysts used in self-cleaning glass, antimicrobial coatings, and other products related to preventing contamination or cleaning the environment are created by dispersing catalyst powder in liquid, which requires controlling the particle size distribution.
In this example, Titanium dioxide was measured using a particle size analyzer.

Analytical Data

SALD-2300 Laser Diffraction Particle Size Analyzer

SALD-2300

The SALD-2300 laser diffraction particle size analyzer is capable of measuring a very wide range of particle diameters, from 17 nm to 2500 μm.
Furthermore, it can be used not only for wet-mode measurements, with powder samples dispersed in liquid, but also for dry-mode measurements of powders as they are.

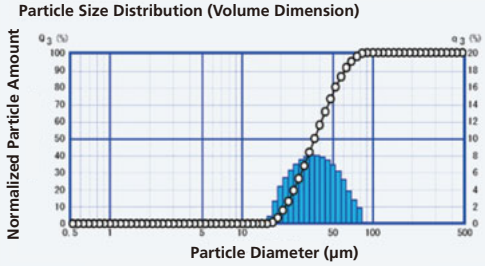


Titanium Dioxide Particle Size Measurement Results (up to 1 μm diameter particles)

IG-1000 Plus Single Nano Particle Size Analyzer

IG-1000 Plus

The IG-1000 Plus uses a new IG (induced grating) measurement principle to analyze particle diameters ranging from 0.5 nm to 200 nm.
In particular, it achieves high reproducibility when measuring particles smaller than 10 nm, which were difficult to measure using conventional dynamic light scattering methods.



Titanium Dioxide Particle Size Measurement Results (particles with diameters in the tens of nm)

Shimadzu Corporation
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